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ACTIVATION OF HYDROPEROXIDES BY $\mathbf{Fe^{II}(MeCN)_4(ClO_4)_2}$ AND $\mathbf{Fe^{III}Cl_3}$ IN ACETONITRILE; MODEL SYSTEMS FOR THE ACTIVE SITES OF *PEROXIDASES*, *CATALASE*, AND *MONOXYGENASES*

Addition of $Fe^{II}(MeCN)_4(ClO_4)_2$ to solutions of hydrogen peroxide in dry acetonitrile catalyzes the rapid disproportionation of H_2O_2 via initial formation of a $Fe^{II}(H_2O_2)^{2+}$ adduct, which, in turn, oxidizes a second H_2O_2 to yield dioxygen. The intermediate of the latter step dioxygenates diphenylisobenzofuran, 9,10-diphenylanthracene, and rubrene, which are traps for singlet-state dioxygen. This intermediate also dioxygenates electron-rich unsaturated carbon-carbon bonds

$[Ph_2C=CPh_2 \longrightarrow 2Ph_2C(O),$
$PhC\equiv CPh \longrightarrow PhC(O)C(O)Ph,$
$\text{cis-}PhCH=CHPh \rightarrow 2PhCH(O)].$

In the presence of organic substrates such as 1,4-cyclohexadiene, 1,2-diphenylhydrazine, catechols, and thiols, the Fe(II)-H_2O_2/MeCN system yields dehydrogenated products (PhH, PhN=NPh, quinones, and RSSR) with conversion efficiencies that range from 100% to 17%. Although the Fe(II) catalyst does not promote the disproportionation of Me_3COOH or *m*-ClPhC(O)OOH, these hydroperoxides are activated for the dehydrogenation of organic substrates. With substrates such as alcohols, aldehydes, methyl styrene, thioethers, sulfoxides, and phosphines, the $Fe^{II}(H_2O_2)^{2+}$ adduct promotes their monoxygenation to aldehydes, carboxylic acids, epoxide, sulfoxides, sulfones, and phosphine oxides, respectively.

$$Fe(II) + H_2O_2 \longrightarrow Fe^{II}(H_2O_2)^{2+} \xrightarrow{RH} Fe(II) + ROH + H_2O$$

The reaction efficiencies for the group of substrates with the Fe(II) adducts that are formed by H_2O_2, Me_3COOH, and *m*-ClPhC(O)OOH have been evaluated. Also, the reaction rates for the substrate-$[Fe^{II}(H_2O_2)^{2+}]$ dehydrogenations and monoxygenations relative to that for Ph_2SO have been determined, as have the substituent effects for the monoxygenation of 4-X-$PhCH_2OH$ and 4-X-PhCH(O). The $Fe^{II}(H_2O_2)^{2+}$ adduct is an efficient catalyst for the autoxygenation of PhCH(O) to PhC(O)OOH. In all of these processes the iron(II) catalyst remains in its reduced state.

Solutions of $Fe^{III}Cl_3$ in dry acetonitrile also catalyze the rapid disproportionation of H_2O_2 to O_2 and H_2O, but the catalyst remains in the Fe(III) state. In the presence of triphenylphosphine, dimethyl sulfoxide, and olefins the $Fe^{III}Cl_3$-H_2O_2/MeCN system yields monoxygenated substrates (Ph_3PO, Me_2SO_2, and epoxides). The epoxidation of olefins is especially favored by the $Fe^{III}Cl_3$-H_2O_2 adduct.

Both of these catalyst systems $[Fe^{II}(MeCN)_4(ClO_4)_2$ and $Fe^{III}Cl_3]$ in dry acetonitrile activate hydroperoxides for the dehydrogenation and monoxygenation of organic substrates, and do not promote radical processes (Fenton chemistry). Their ability to facilitate these reactions via the oxene chemistry of ferryl (FeO^{2+}) and perferryl ($FeCl_3O$) make them useful reaction mimics for the active sites of *peroxidases*, *catalase*, and *monoxygenases*.

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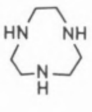
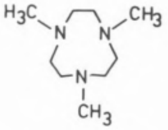
SYNTHESES OF IRON MODEL COMPOUNDS WITH MACROCYCLIC *N*-DONOR LIGANDS

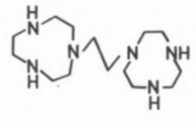
Small macrocyclic *N*-donor ligands have been used to assemble inorganic model compounds for the met form of vertebrate respiratory protein hemerythrin from mononuclear Fe^{III} complexes. These ligands include the following examples:



tcn



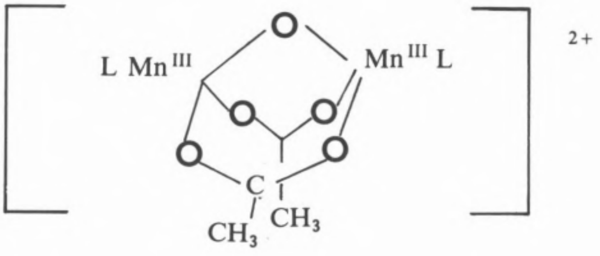
mtcn



dtcn

A series of iron(III) complexes containing the (μ-oxo)bis(μ-carboxylato)diiron(III) core with the above ligands have been synthesized and characterized by X-ray crystallography. Their spectroscopic and magnetic properties are compared with the natural proteins. The reactivity of the core has also been investigated. The reactions of the model compounds with N_3^-, NCS^- *etc.* afford binuclear oxo-bridged species, *e.g.* $[(tcn)(N_3)_2Fe\text{-}O\text{-}Fe(N_3)_2(tcn)]$, and $[(tcn)Fe(N_3)_3]$ indicating the facile degradation of the (μ-oxo)-bis(carboxylato) unit.

Analogous compounds containing Mn^{III} have also been prepared. Their structures, spectroscopic, magnetic and chemical properties will be briefly discussed.



The mixed valence Mn^{III} Mn^{IV} binuclear complexes are readily obtained by oxidation of the above complex with $AgBF_4$ in acetonitrile. These complexes may serve as models for the water-oxidation enzyme photosystem II.

Finally, an octameric cation, $[Fe_8(tcn)_6(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}]^{8+}$, has been prepared and characterized by X-ray crystallography. The quantitative assembly of this species in aqueous solution at ambient temperature and pH 7-8 starting from mononuclear $(tcn)FeCl_3$ may serve as a model reaction for the iron storage protein ferritin.